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THE WETTING BEHAVIOR OF YTTRIA-ALUMINA-SILICA ADDITIVES FOR PRE-ETC(U)

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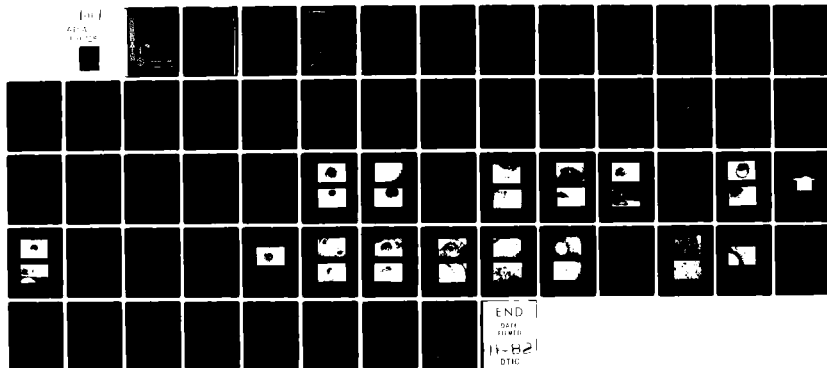
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**THE WETTING BEHAVIOR OF YTTRIA-ALUMINA-  
SILICA ADDITIVES FOR  
PRESSURELESS SINTERING OF SILICON NITRIDE**

Alan D. Miller

April 1982

University of Washington  
College of Engineering  
Ceramic Engineering Division

Final Report- July 1979 - January 1981

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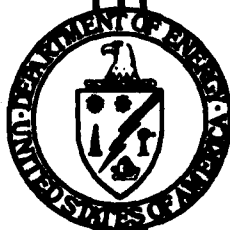
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**U. S. DEPARTMENT OF ENERGY**

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ABSTRACT

The aims of this study were to observe and measure the wetting behavior of liquid yttria-alumina-silica mixtures when in contact with silicon nitride at high temperature and in an environment of one atmosphere of nitrogen. Preliminary indications suggest that over a wide range of yttrium contents, the wettability range is small and that the compositions are reactive to the substrate even though they do not wet readily. A much larger experimental data base is necessary, however, over a wider range of experimental conditions to understand the wetting characteristics and reaction behavior in this complex system.

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## FORWARD

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## I. Introduction

### A. Objectives

The general aims of this study were to observe and measure the wetting behavior of liquid yttria-alumina-silica mixtures when in contact with silicon nitride at high temperature and in an environment of one atmosphere of nitrogen. The ultimate goal is to develop information which will lead to improved sintering aids to be used in the "pressureless", i.e., one atmosphere nitrogen, sintering of silicon nitride. The study employed two classes of experiments.

The first experiment involved preparing specimens of reaction bonded silicon nitride (RBSN) with no sintering-aid additions. The interaction between these specimens and selected pre-reacted yttria-alumina-silica mixtures was studied by placing the components in contact and heating to temperatures of interest. The specimens were examined by optical and electron microscopy and by x-ray diffraction and microspectroscopy to determine the nature and extent of the penetration of the additive into the RBSN specimen.

The second experiment was more fundamental. Specimens of the same pre-reacted yttria-alumina-silica mixtures were placed on a substrate of polished chemically-vapor-deposited (CVD) silicon nitride, at temperatures at which the oxide mixture was molten, and allowed to equilibrate. The wetting angle of the sessile drop so formed was measured simply by cooling the furnace relatively rapidly and examining the specimen at room temperature.

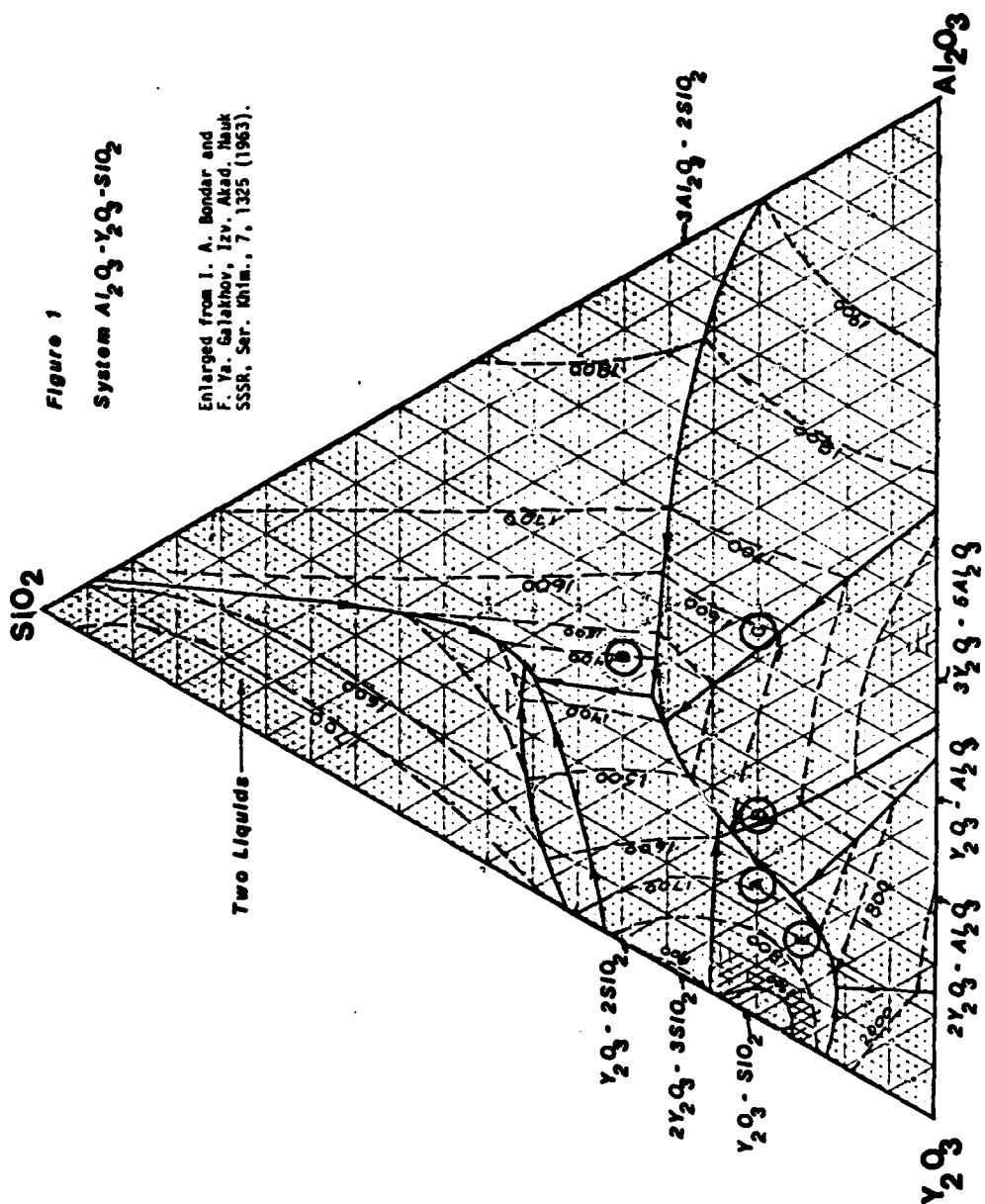
## B. Scope of the Work

The experiments reported on herein were conducted by additives of the following compositions (in weight percent):

- A. 67%  $Y_2O_3$  - 13%  $Al_2O_3$  - 20%  $SiO_2$
- B. 60%  $Y_2O_3$  - 20%  $Al_2O_3$  - 20%  $SiO_2$
- C. 42%  $Y_2O_3$  - 38%  $Al_2O_3$  - 20%  $SiO_2$
- D. 37%  $Y_2O_3$  - 28%  $Al_2O_3$  - 35%  $SiO_2$
- E. 75%  $Y_2O_3$  - 15%  $Al_2O_3$  - 10%  $SiO_2$

The area of interest is indicated on the phase equilibrium diagram of Figure 1. It will be noted that many of the compositions have 20 weight percent silica. Yttria-alumina compositions were of primary interest but it is recognized that all silicon nitride powders contain oxygen, typically in amounts equivalent to two weight percent silica. If it is assumed that the silica is present on particle surfaces and that it dissolves in the liquid additive phase at the sintering temperature, then a typical 10 weight percent addition of yttria-alumina would contain approximately 20 weight percent silica at the firing temperature. Details of the selection of additive compositions are discussed in Section III.A.

The temperatures investigated were limited by the liquidus surface of the  $Y_2O_3$  -  $Al_2O_3$  -  $SiO_2$  system at the particular composition in



question and a temperature at which the decomposition pressure of silicon nitride becomes high enough to give unacceptable weight losses. Thus the temperatures were in the range of 1650 to 1800°C.

## II. Literature Background

A number of additives have been used to promote densification of silicon nitride during the process of sintering or hot pressing. These additives are necessary since the bulk and grain boundary diffusion coefficients are very low, leading to essentially zero densification rates under completely solid-state processes. The presence of a reactive liquid phase which both dissolves and wets the silicon nitride particles is required.

A number of oxides have been used as densification aids. The following studies are examples: The work of Mitomo (1) on MgO, Gazza (2) on  $Y_2O_3$ , Priest et al. (3) on  $CeO_2$ , Bowen et al. (4) on  $Li_2O$  and Mitomo (1) on  $Al_2O_3$ . Early studies found MgO to be a better additive than others considered. Although MgO produced dense, high strength  $Si_3N_4$ , the material exhibits a decrease in strength at high temperatures and subcritical crack growth at temperatures above approximately 125°C. The decrease in high temperature properties has been attributed to the boundary phase which at high temperatures becomes viscous and may allow grain boundary sliding. As research continued on  $Si_3N_4$ , MgO became the most studied additive. Terwilliger and Lange (5), Mitomo (1), and Amato et al. (6) discuss the mechanisms and kinetics of densification with MgO. Greskovich and O'Clair (7) reported that impurities,

e.g., Ca, Fe and Al, enhance the sintering of  $\text{Si}_3\text{N}_4$  with MgO.

Richerson (8) investigated how the impurities affected the refractoriness of the MgO bond phase and showed that as the general impurity level increased, the high temperature strength decreased. While hot pressed and sintered  $\text{Si}_3\text{N}_4$  with MgO showed high density and high room temperature strength, the decrease in high temperature strength--marked by lower creep resistance and subcritical crack growth above approximately 1250°C was undesirable. Apparently the MgO forms a glassy boundary phase, which becomes viscous and slides at high temperatures. This grain boundary problem worsens with increasing impurities which concentrate in the grain boundary silicate phase.

After identifying the silicate's detrimental effects there were two approaches to improving high temperature properties of silicon nitride:

- (1) Minimize the glassy phase by decreasing impurities and decreasing the amount of MgO additive, or
- (2) Form a more refractory intergranular phase by using alternative additives and possibly crystallize the glassy boundary phase.

Yttria, a rare earth oxide, has been an effective replacement for magnesia. Gazza (2,9) used yttria which reacted with surface  $\text{SiO}_2$  on the  $\text{Si}_3\text{N}_4$  to form a more refractory boundary phase. The addition of yttria,  $\text{Y}_2\text{O}_3$ , gives high density and high strength at elevated temperatures. Tsuge et al. (10) describe a presintering step to 1600 or 1700°C before hot pressing  $\text{Si}_3\text{N}_4$  in order to make a crystalline phase ( $\text{Si}_3\text{N}_4\text{Y}_2\text{O}_3$ ) with a high liquidus temperature (~1850°C). The

crystalline second phase is effective when it has a melting point greater than the  $\text{Si}_3\text{N}_4$  decomposition temperature ( $1870^\circ\text{C}$ ). Wills et al. (11) studied the phase relationships between  $\text{Y}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  in hot pressing  $\text{Si}_3\text{N}_4$  and suggested the initial liquid densification aid was a silica rich  $\text{Si}_3\text{N}_4$ - $\text{SiO}_2$ - $\text{Y}_2\text{O}_3$  liquid below  $1600^\circ\text{C}$ . At higher temperatures the liquid becomes richer in  $\text{Si}_3\text{N}_4$  and  $\text{Y}_2\text{O}_3$  since the amount of  $\text{SiO}_2$  is limited. Clark (12), in a grain boundary study of  $\text{Y}_2\text{O}_3$  in hot-pressed  $\text{Si}_3\text{N}_4$ , reported 3 phases-- $\text{Si}_3\text{N}_4$ , yttrium-silicon oxynitride, and an unidentified thin interphase layer. The yttrium-silicon oxynitride phase dissolves impurity elements into solid solution in the grain boundary. Rae et al. (13) describe  $\text{Si}_3\text{N}_4$  densification initiating with a yttria-silica-nitride reaction which produces a liquid phase and densification continues as  $\text{Si}_3\text{N}_4$  and the liquid combine to give one or more refractory phases. Impurities which concentrated in the glassy phase with  $\text{MgO}$  appear to become part of the refractory phases with  $\text{Y}_2\text{O}_3$ . Krivanek (14) observed thin intergranular glassy films in sintered silicon nitride and concluded that these glassy phases were responsible for high temperature strength degradation. The glassy phases are due to additives and impurities introduced during processing.

A major problem with the use of  $\text{Y}_2\text{O}_3$  as an additive involves the presence of certain secondary phases which oxidize readily with accompanying large molar volume change. Polyphase materials with the unstable secondary phases were observed by Lange et al. (15) to crack apart after short oxidation times at  $\approx 1000^\circ\text{C}$ , in some cases degrading to a powder. It was found through phase equilibria work that



these problems could be averted by using compositions within the  $\text{Si}_3\text{N}_4\text{-Si}_2\text{ON}_2\text{-Y}_2\text{Si}_2\text{O}_7$  compatibility triangle as described by Lange et al. (15). These compositions avoid the unstable phases and have proved to exhibit the most advantageous high temperature mechanical properties and oxidation resistance observed to date for  $\text{Si}_3\text{N}_4$  alloys as reported in a review by Lange (16).

Impurities such as W, C, Fe, Ca, Al enhance sintering. However, they are a disadvantage because they interfere with crystallization of the intergranular phase. Knoch and Gazza (17) found that carbon impurities from milling media and the graphite die degrade oxidation resistance at  $\sim 1000^\circ\text{C}$ . Smith and Quackenbush (18) report on the deleterious effect of  $\text{Al}_2\text{O}_3$  on  $\text{Si}_3\text{N}_4$  sintered with  $\text{Y}_2\text{O}_3$  additives and show increased high temperature ( $> 1200^\circ\text{C}$ ) strength as the amount of  $\text{Al}_2\text{O}_3$  decreases. Galasso and Veltri (19) concluded that  $\text{Al}_2\text{O}_3$  increased sintered densities of  $\text{Si}_3\text{N}_4$  but oxidation resistance and bend strength.

For liquid phase sintering with an additive there must be an appreciable amount of liquid, the solid must dissolve in the liquid phase, and the liquid must wet the solid phase. The origin of this sintering enhancement by certain additives and impurities is not yet well known, but may be due to:

- 1) increased volume of liquid phase,
- 2) enhanced solubility of  $\text{Si}_3\text{N}_4$  in the liquid phase,
- 3) decreased viscosity of the liquid phase, and
- 4) increased wetting by the liquid phase of  $\alpha\text{-Si}_3\text{N}_4$  grain interfaces (Greskovich and O'Clair (7)).

Kingery (20) discusses the three generally agreed upon stages in liquid phase sintering:

- 1) Formation of a liquid and initial particle rearrangement.
- 2) Solution of the solid phase in the liquid, followed by precipitation.
- 3) Coalescence, the development of a solid framework that slows the rate of densification.

Although wetting is mentioned in the  $\text{Si}_3\text{N}_4$  literature, there is a relative lack of experimentation. Whalen and Humenik (21) pointed out that good wetting of the solid phase by the liquid phase during sintering must occur in order to sinter successfully with a liquid phase.

The most thorough wetting study of  $\text{Si}_3\text{N}_4$  was done by Kossowsky (22). He studied the wetting characteristics of enstatite ( $\text{MgSiO}_3$ ) and alkaline-doped enstatite on  $\text{Si}_3\text{N}_4$ , and the nature of the glass-solid interface. The alkaline-doped  $\text{MgSiO}_3$  was added to simulate the effect of impurities such as  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ . The x-ray diffraction data showed that small additions of alkaline oxides to pure  $\text{MgSiO}_3$  result in multiple phase mixtures in which enstatite becomes a minor phase. Complete wetting of the high purity hot pressed  $\text{Si}_3\text{N}_4$  sample was not achieved with liquid of the enstatite composition alone; the simulated impurity additions were required. Studies of the glass -  $\text{Si}_3\text{N}_4$  interface by scanning electron microscopy showed that the magnesium, and to some extent the calcium, diffused into the  $\text{Si}_3\text{N}_4$  substrate. When observing the development of wetting as a function of time under isothermal conditions, no detectable time effect was shown for

$\text{MgSiO}_3 \cdot \text{Si}_3\text{N}_4$  at  $1720^\circ\text{C}$ . Because the alkaline impurities improve the wetting of magnesium silicates on  $\text{Si}_3\text{N}_4$  but contribute to a decrease in high temperature strength, it was suggested that 50 to 100 ppm alkaline impurities may be optimal.

### III. Experimental Procedures

#### A. Additive Materials

The additive compositions shown in Table I were arrived at by considering sintering aid additions at a ten weight percent level. The lowest reasonable oxygen levels, expressed as percent by weight silica, in silicon nitride powders was considered to be 2%. This assumption is supported by reported oxygen levels of 2.6 and 1.1 weight percent for two common silicon nitride powders.\* The additives in the experiments reported here receive little silica contribution to their composition from oxygen in the  $\text{Si}_3\text{N}_4$  due to the nature of the experiment. Therefore silica was added to the yttria-alumina to model that received from oxygen in powder compacts. Three compositions were chosen so as to contain 20 weight percent  $\text{SiO}_2$ . This corresponds to the approximate  $\text{SiO}_2$  concentration in an additive, initially free of  $\text{SiO}_2$  and added at the 10% level, which has absorbed all of a 2%  $\text{SiO}_2$  impurity on the surface of the  $\text{Si}_3\text{N}_4$  grains.

---

\*GTE Sylvania SN502 and H. Stark  $\text{Si}_3\text{N}_4$ , respectively.

TABLE I

$Y_2O_3$ - $Al_2O_3$ - $SiO_2$  Compositions (W/O) on Which Wetting Studies  
Were Conducted

A. 67% $Y_2O_3$ - 13% $Al_2O_3$ - 20% $SiO_2$	$T_L = 1700^\circ C$
B. 60% $Y_2O_3$ - 20% $Al_2O_3$ - 20% $SiO_2$	$T_L = 1630^\circ C$
C. 42% $Y_2O_3$ - 38% $Al_2O_3$ - 20% $SiO_2$	$T_L = 1600^\circ C$
D. 37% $Y_2O_3$ - 28% $Al_2O_3$ - 35% $SiO_2$	$T_L = 1400^\circ C$
E. 75% $Y_2O_3$ - 15% $Al_2O_3$ - 10% $SiO_2$	$T_L = 1750^\circ C$

( $T_L$  = liquidus temperature)

Varying amounts of yttria and alumina were added to the 20% silica compositions subject to the criteria that the melting point of the additive be  $1700^\circ C$  or less and the alumina content be less than 50%. (Equivalent to less than 5%  $Al_2O_3$  in a  $Si_3N_4$  compact with 10% additives.) Composition D was chosen on the basis of encouraging results obtained with composition C. The fifth composition (E) was chosen as a low  $SiO_2$ , low  $Al_2O_3$  composition with fairly low liquidus temperature, even though greater than  $1700^\circ C$ .

The raw materials used to prepare the additive compositions are shown in Table II. The additive compositions were pre-reacted to insure homogeneity and to prevent local non-equilibrium melting. Five gram batches of each composition were formulated and fired in closed boron nitride crucibles. The crucibles and lids were machined from hot-pressed boron nitride rod.\* Each composition was heated to at

\*Carborundum Co., Niagara Falls, NY, Grade A.

TABLE II.

## Raw Materials Used in Preparation of Additives

Material	Supplier and	Purity	Particle Size
	Supplier Designation	Vendor Analysis	Vendor Analysis
Y <sub>2</sub> O <sub>3</sub>	Cerac Y-1037*	Typ. 99.9% Y <sub>2</sub> O <sub>3</sub> ± 1% Rare earth Other cation < 10ppm	-325 Mesh
Al <sub>2</sub> O <sub>3</sub>	Linde "A"***	99.95 Al <sub>2</sub> O <sub>3</sub> No cation > 100 ppm	0.3 µm ave surface area 14.5 m <sup>2</sup> /g
SiO <sub>2</sub>	Imsil A-10***	99.5 + 0.5 SiO <sub>2</sub> Major impurities CaO 0.15% Fe <sub>2</sub> O <sub>3</sub> 0.025% LOI 0.3%	99% < 10 µm 76% < 5 µm 1.46 m <sup>2</sup> /g

\*Cerac, Inc., Milwaukee, Wisconsin

\*\*Union Carbide Corp., Linde Division, Indianapolis, Indiana

\*\*\*Illinois Minerals, Cairo, Illinois

least 50°C above the liquidus temperature indicated by the phase equilibrium diagram in Figure 1, then held at temperature for one hour. In no case was the pre-reaction temperature less than 1675°C. The atmosphere external to the crucible was argon - 10% nitrogen. Essentially all of the weight loss could be directly attributed to the crucible and not to the additive. It is believed that there was no significant compositional change to any of the additive batches during the pre-reaction firing with the exception of 75% Y<sub>2</sub>O<sub>3</sub> - 15% Al<sub>2</sub>O<sub>3</sub> - 10% SiO<sub>2</sub>. The higher firing temperature (1800°C) is believed to have resulted in some BN dissolution in the molten additive.

After the heat treatment the additives were ground to pass a 200 mesh sieve. These powders were analyzed by x-ray diffraction and used for making specimens for the sessile drop test and for the RBSN penetration tests.

The x-ray diffraction analysis of reacted additive compositions yielded the results shown in Table III. All of these phases are shown on the phase equilibrium diagram except for the phase labeled  $Y_{4.67}(SiO_4)_3O$  which is described in the standard pattern as a "product of oxidation of the  $Y_5(SiO_4)_3N$  phase of apatite structure type."

#### B. Sessile Drop Experiments

The substrate plates for the sessile drop experiments were fabricated from high purity CVD  $\alpha$ - $Si_3N_4$ \*. The CVD material was received from the source still attached to the graphite growth substrate. The graphite-silicon nitride plates were cut into approximately 2.5 cm squares and the graphite oxidized away by heating at 830°C for 16 hours in air. The  $Si_3N_4$  was then ground flat using a 400 grit diamond wheel and polished on a vibratory polisher using 0.3 micrometer aluminum oxide on silk for 48 hours. This procedure gave flat plates with a mirror finish. The 2.5 cm squares were then cut to approximately 1.2 cm square for the sessile drop experiment.

Small pellets of ground additive were formed by pressing the powder in 3.2 mm I.D. Tygon tubing using steel plungers. After

---

\*General Electric Co., Space Systems Division, Philadelphia, PA.

TABLE III.

Phases Present in Pre-Reacted Additives by X-Ray Diffraction Analysis

Additive	Phases Present	
A. (67Y-13A-20S)*	$3Y_2O_3 \cdot 5Al_2O_3$ $Y_2O_3 \cdot SiO_2$	$\beta - Y_2O_3 \cdot 2SiO_2$
B. (60Y-20A-20S)		$Y_2O_3 \cdot SiO_2$ $\beta - Y_2O_3 \cdot 2SiO_2$
C. (42Y-38A-20S)	$3Y_2O_3 \cdot 5Al_2O_3$	$\beta - Y_2O_3 \cdot 2SiO_2$
	$\alpha - Al_2O_3$	$\alpha - Y_2O_3 \cdot 2SiO_2$
D. (37Y-28A-35S)	No crystalline pattern; characteristic amorphous "hump"	
E. (75Y-15A-10S)	$Y_{4.67}(SiO_4)_3O$	$Y_2O_3 \cdot SiO_2$
	$3Y_2O_3 \cdot 5Al_2O_3$	$2Y_2O_3 \cdot Al_2O_3$
	$YBO_3$	

\*Y =  $Y_2O_3$ A =  $Al_2O_3$ S =  $SiO_2$ 

Compositions in wt. percent.

prepressing, the dies were enclosed in a latex bag and isostatically pressed to 200 MPa (30 ksi). This produced very uniform right circular cylinders which had sufficient integrity with no binder added that they could be handled, albeit with some care needed.

After weighing, the pellet was set on the CVD  $\text{Si}_3\text{N}_4$  setter and this in turn placed on a graphite platform in the test furnace.

Once loaded, the furnace was evacuated to less than 5 Pa (40 micrometers Hg) and backfilled with argon. The argon was brought to one atmosphere pressure and allowed to escape slowly through a vacuum oil bubbler. Nitrogen was then introduced at a flow rate approximately one-tenth that of the argon, the total flow rate being approximately  $1.5 \times 10^{-5} \text{ m}^3/\text{sec}$  ( $15.4 \text{ cm}^3/\text{sec}$ ). A typical furnace run was as follows: heat at  $300^\circ\text{C}$  per hour, hold at temperature for 5-10 minutes and cool at  $600^\circ\text{C}$  per hour. (Temperatures were measured with a calibrated optical pyrometer corrected for sight glass losses.)

Small weight losses, less than 2 milligrams, were noted on most runs. This corresponds to less than 4 percent of the sessile drop mass or 0.4 percent of the combined mass of drop and setter.

The specimens, after removal from the furnace, were photographed at low magnification (1X to 4X on 35 mm film) for general observation. The specimens were also photographed in silhouette at 8X magnification. One photo was taken from a random azimuthal position, the drop was then rotated  $90^\circ$  and a second photograph taken. The contact angle was measured directly from enlarged prints using a protractor.

After photographic documentation, the sessile drop, if not strongly wetting, was separated from the substrate. Additional photographs were then taken of the substrate. X-ray diffraction analysis was performed on the substrate and the sessile drop. The substrate and any material adhering to it were placed in the diffractometer without any sample preparation. Two diffraction patterns were taken with the



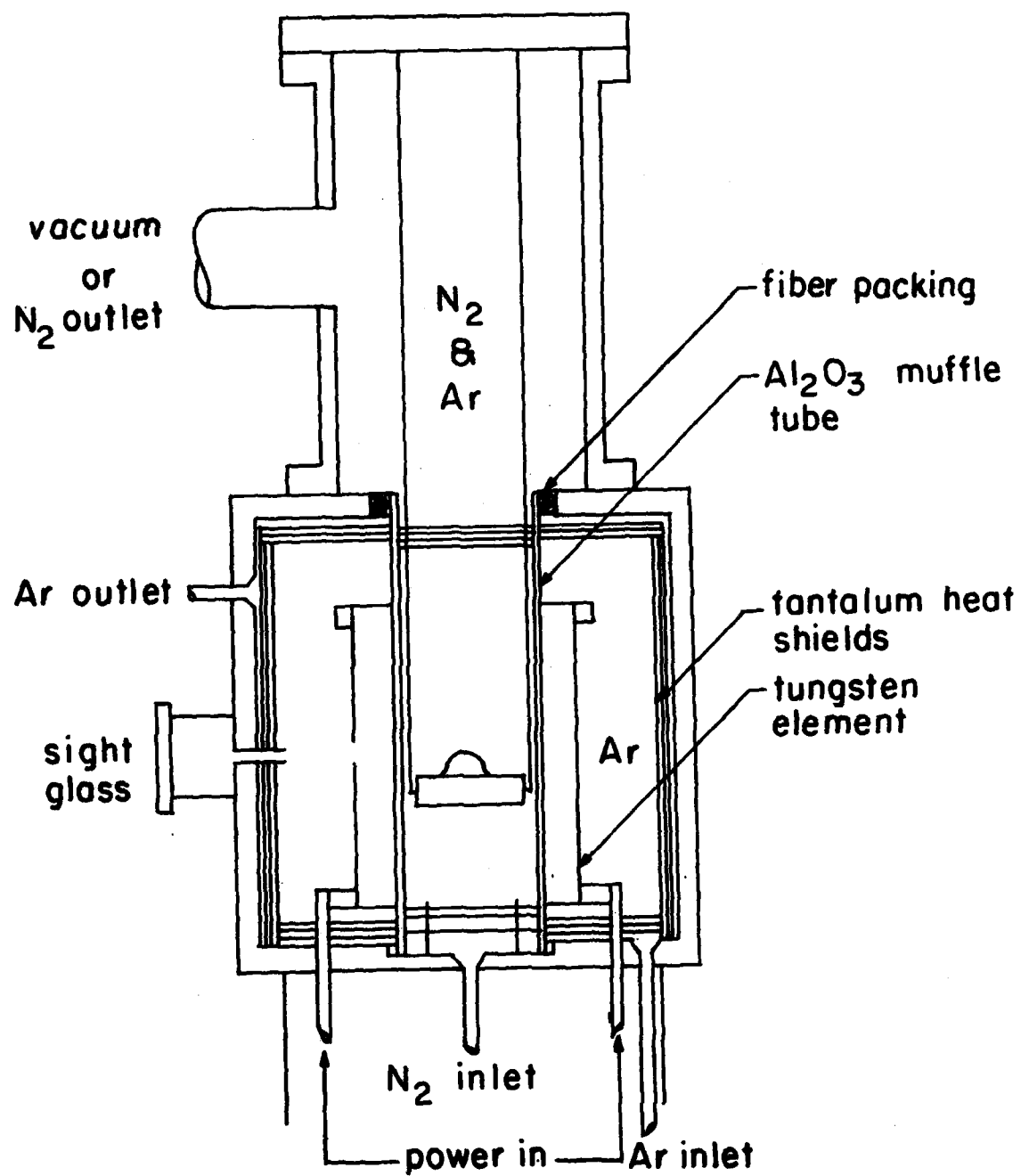


Figure 2. Centorr Furnace

substrate rotated 90° in the sample holder for the second pattern to reduce orientation effects. The drop was crushed, ground and analyzed by normal powder diffractometry techniques.

The furnace used in the study was a tantalum element cold wall vacuum or inert atmosphere furnace utilizing an aluminum oxide tube to isolate the specimen chamber from the heating elements.\* A schematic cross section of the furnace and fixtures is shown in Figure 2.

### C. Penetration Studies

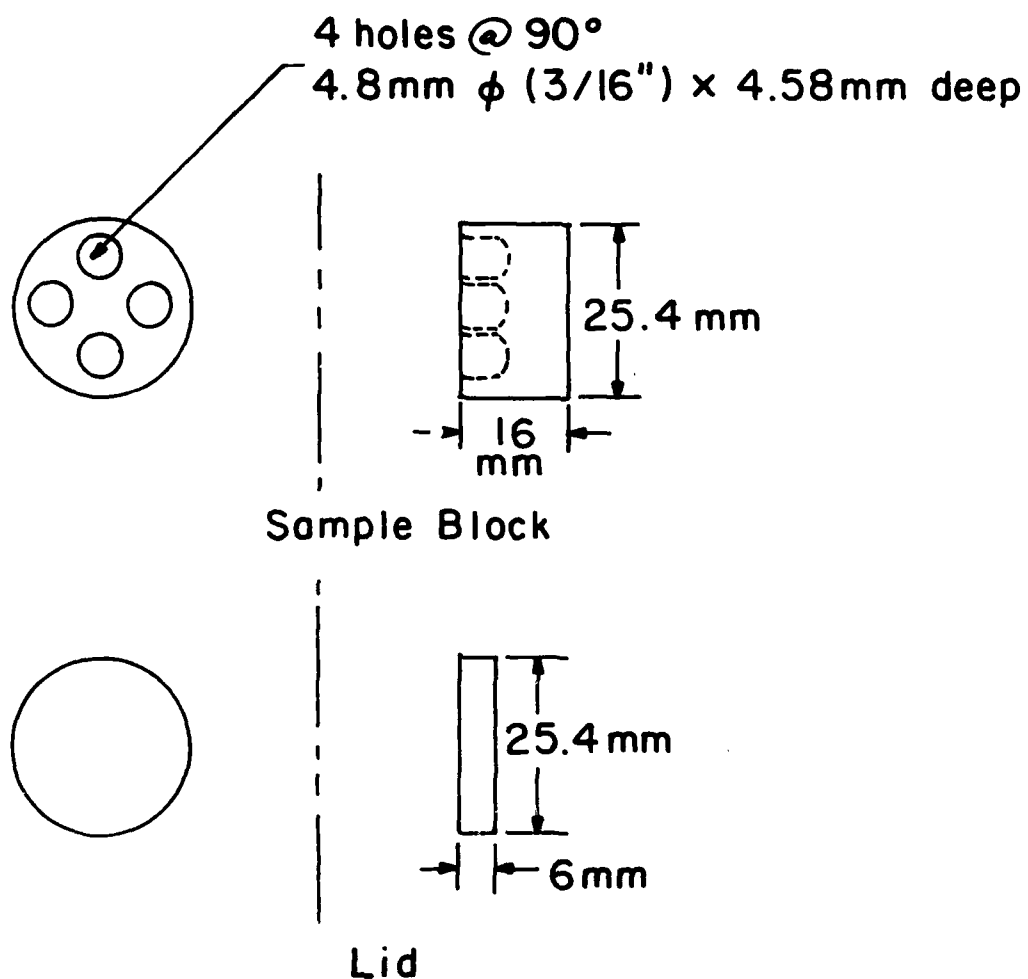
The additive penetration studies were performed using specimens of reaction bonded silicon nitride in the form shown in Figure 3. These specimen blocks were prepared from -200 mesh metallurgical grade silicon metal\*\* which was dry milled in a porcelain jar mill with alumina balls for 24 hours. The milled silicon powder contained approximately 0.6 weight percent iron and 0.4 weight percent  $Al_2O_3$  introduced during milling. The blocks were formed by pressing in steel dies without binder at 17.5 MPa (2550 psi) and then isostatically pressed in a latex bag to 103 MPa (15,000 psi). The silicon discs were nitrided in a molybdenum element nitriding furnace\*\*\* equipped with nitrogen demand control. The nitriding schedule was as shown in Figure 4.

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\*Centorr Model 15 Laboratory Furnace, Centorr Associates, Suncook, NH.

\*\*Union Carbide Corporation.

\*\*\*Brew Model 801-4S, R.D. Brew & Company, Concord, NH.



Scale: full size  
material: RBSN

Figure 3. Penetration Specimen Block

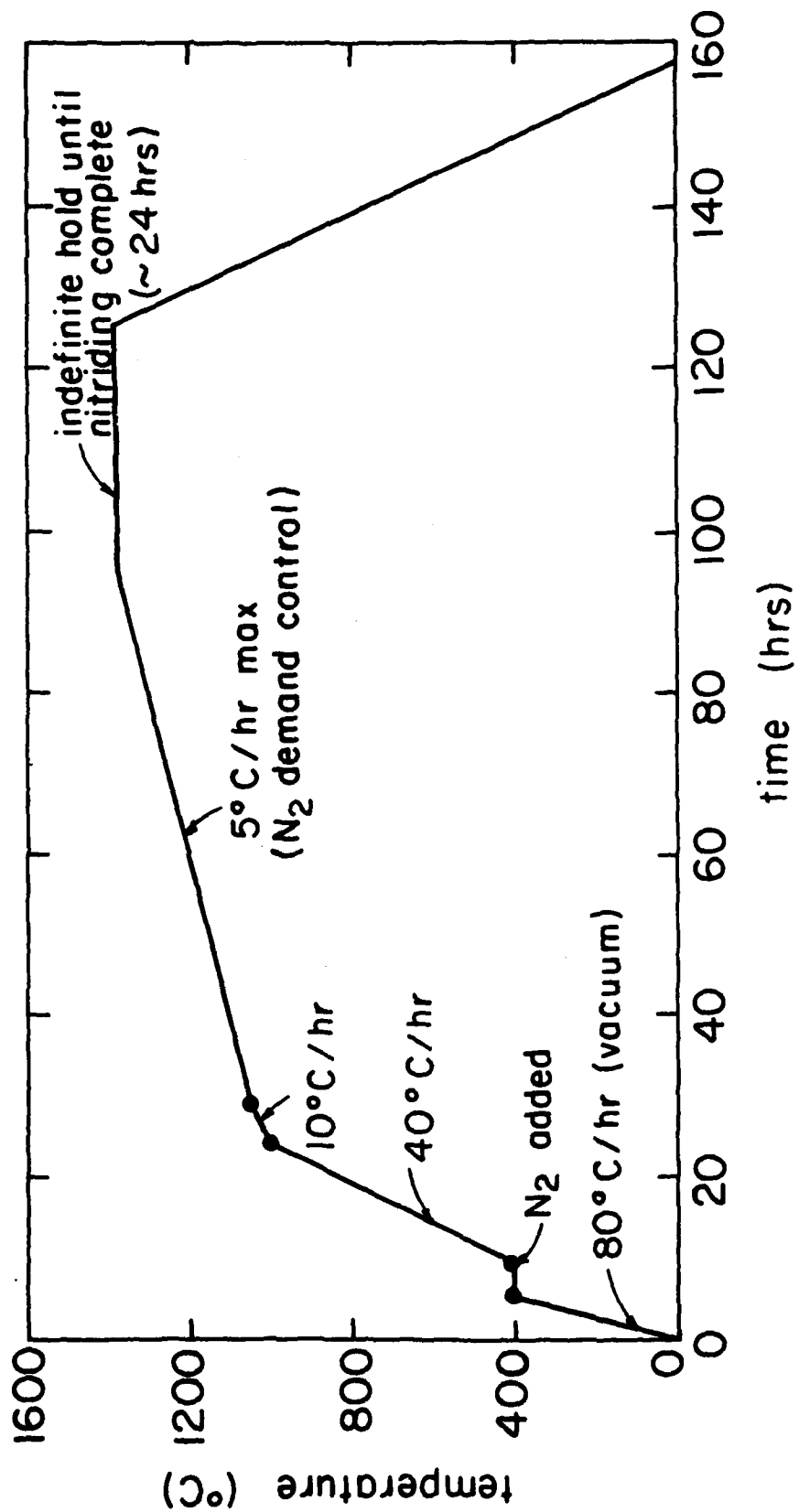


Figure 4. Nitriding Schedule

Based on weight gain of the specimen blocks during nitriding, 97% of the silicon was converted to nitride. The presence of iron and aluminum oxide was not taken into account in these calculations hence the percent nitride conversion was higher. No indication of any free silicon was seen in subsequent analysis of the specimen blocks.

Upon removal from the nitriding furnace, the blocks were sliced with a diamond saw to provide a lid. The 4.8 mm sample cavities were drilled using a diamond dental burr. The blocks were then preconditioned by heating in argon-nitrogen to 1400°C for one hour.

The specimen assembly was prepared by packing a small amount of the additive powder into the cavities in the block, placing the lid over the cavity and positioning the entire assembly in the tantalum resistance furnace previously described. The temperature was raised to the desired level at a rate of 300°C per hour and held at the maximum for one hour. The furnace was then cooled at a rate of 300-500°C per hour to 400°C then turned off. Temperatures were measured with a disappearing filament optical pyrometer calibrated against an NBS certified standard lamp and corrected for sight-glass losses. Upon removal from the furnace the specimens were examined visually and low power photographs were taken. The specimens were then sectioned for examination by optical microscopy. Polished sections were prepared by the usual techniques. Vibratory polish using 0.6 micrometer diamond on silk was used as a final step. Alumina was not used as a final polishing medium since x-ray micro-spectrographic analysis for aluminum was planned.

The specimens were examined by reflected light microscopy, x-ray microspectroscopy, and scanning electron fractography. Each of these will be discussed in detail in the section on results.

#### IV. Results and Discussion

##### A. Results of the Sessile Drop Experiments

Seven sessile drop experiments were conducted on four separate additive compositions. The basic observations made on the specimens are shown in Table IV. The last experiment shown used a polished surface of reaction-bonded silicon nitride prepared as described in the procedures section.

Specimen A ( $67Y_2O_3$ - $13Al_2O_3$ - $20SiO_2$ ) formed the nearly spherical drop shown in Figure 5. The drop was opaque and crystalline in appearance with the contact angle measured as  $101^\circ$  and  $132^\circ$  in the two measurements  $90^\circ$  apart. A white reaction zone of approximately twice the diameter of the drop surrounded the drop. This zone appeared to be a thin coating on the substrate. This zone is shown in more detail in Figure 6a. X-ray diffraction analysis of the ground drop showed the same crystalline species as were present in the drop before the experimental run. There were, however, three additional lines in the pattern which could not be identified. Diffraction analysis of the substrate showed the CVD  $Si_3N_4$  pattern plus additional lines. The additional lines were distinct, but could not be correlated with any phase or combination of phases.

TABLE IV

## Results of Sessile Drop Experiments

Specimen A -- 67  $Y_2O_3$  - 13  $Al_2O_3$  - 20  $SiO_2$ 

Liquidus: 1700°C  
 Temperature/Time: 1730°C for 7 minutes  
 Cooling Rate: 21°/min to 1635°C  
                   8°/min to 1290°C  
 Weight Loss: 2.1 mg  
 Contact Angle: 101-132°, nonwetting

Specimen B1 -- 60  $Y_2O_3$  - 20  $Al_2O_3$  - 20  $SiO_2$ 

Liquidus: 1630°C  
 Temperature/Time: 1700-1720°C for 10 minutes  
 Cooling Rate: 35°/min to 1350°C  
 Weight Loss: 1.5 mg  
 Contact Angle: 28-43°, wetting

Specimen B2 -- 60  $Y_2O_3$  - 20  $Al_2O_3$  - 20  $SiO_2$ 

Liquidus: 1630°C  
 Temperature/Time: 1730°C for 5 minutes  
 Cooling Rate: 24°/min to 1575°C  
                   9°/min to 1000°C  
 Weight Loss: 1.0 mg  
 Contact Angle: 16-30°, wetting

Specimen C1 -- 42  $Y_2O_3$  - 38  $Al_2O_3$  - 20  $SiO_2$ 

Liquidus: 1600°C  
 Temperature/Time: 1705°C for 5 minutes  
 Cooling Rate: 35°/min to 1630°C  
                   7°/min to 1000°C  
 Weight Loss: 0.4 mg  
 Contact Angles: Crystalline Drop 142-153°  
 (Phase separation) Second Phase 47-62°

TABLE IV--continued

Specimen C2 -- 42  $Y_2O_3$  - 38  $Al_2O_3$  - 20  $SiO_2$

Liquidus: 1600°C  
Temperature/Time: 1705°C for 65 minutes  
Cooling Rate: 35°/min to 1350°C  
8°/min to 975°C  
Weight Loss: 1.5 mg  
Contact Angle: 122-162°  
(No phase separation)

Specimen D1 -- 37  $Y_2O_3$  - 28  $Al_2O_3$  - 35  $SiO_2$

Liquidus: 1400°C  
Temperature/Time: 1700°C for 12 minutes  
Cooling Rate: 10°/min to 970°C  
Weight Loss: 0.0 mg  
Contact Angle: 33-48°

Specimen D2 -- 37  $Y_2O_3$  - 28  $Al_2O_3$  - 35  $SiO_2$

RBSN Substrate

Liquidus: 1400°C  
Temperature/Time: 1710-1725°C for 25 minutes  
Cooling Rate:  
Weight Loss: 3.8 mg  
Contact Angle: 96-106°



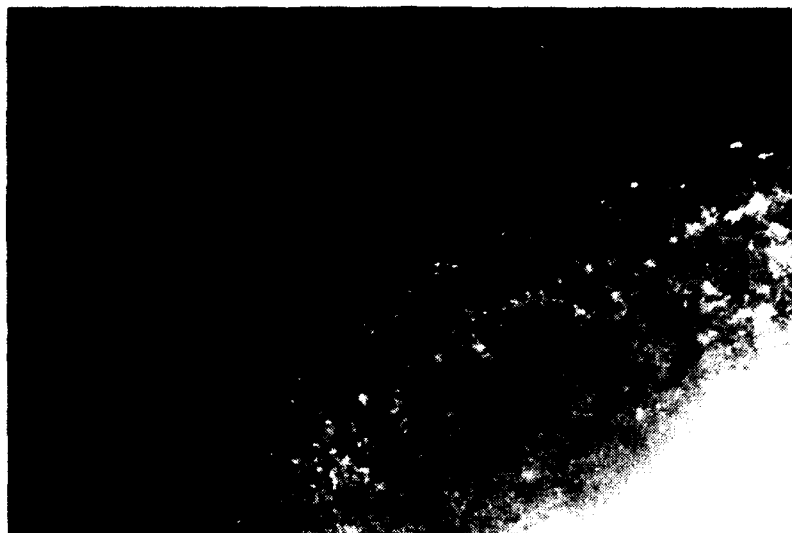


(13x)



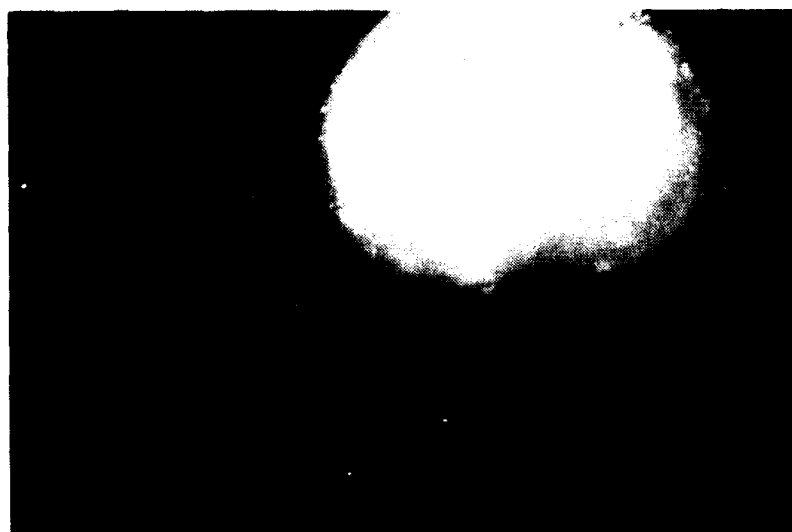
(13x)

Figure 5. Sessile Drop Specimen A  
 (67  $Y_2O_3$  - 13  $Al_2O_3$  - 20  $SiO_2$ )



a. Note apparent reaction with substrate

(26x)



b. Shows large wetting angle

(13x)

Figure 6. Sessile Drop Specimen A  
(67  $\text{Y}_2\text{O}_3$  - 13  $\text{Al}_2\text{O}_3$  - 20  $\text{SiO}_2$ )

The additive of Specimen B1 ( $60Y_2O_3-20Al_2O_3-20SiO_2$ ) wet the CVD substrate with measured contact angles of  $28^\circ$  and  $43^\circ$ . A portion of the drop is shown in Figure 7. The pitted and cratered surface of the drop are suggestive of a gas-phase evolution during the test. As noted in Table IV, however, no abnormal weight loss was seen. X-ray diffraction analysis of the drop material showed the same phases as the pre-test analysis while the substrate patterns showed the CVD substrate and  $\beta-Y_2Si_2O_7$  with a trace of yttrium-aluminum garnet (YAG) phase. Both of these are equilibrium phases to be expected upon cooling a melt of this composition. No extraneous unidentified lines appeared in either pattern.

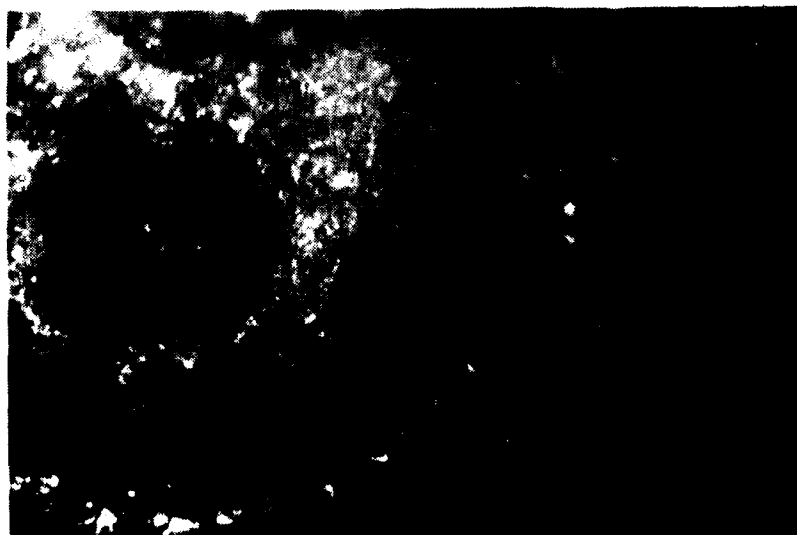
A second specimen of the same composition designated B2 was run under similar conditions as noted in Table IV. Again the additive wet the CVD substrate. In all respects the two runs were similar. Figure 8 shows a silhouette and a normal view of the drop illustrating the wetting behavior and, again, the pitting or bubbling of the drop.

Specimen C1 of composition  $42Y_2O_3-38Al_2O_3-20SiO_2$  showed a much different behavior than the previous specimens. Under the conditions indicated in Table IV the sessile drop showed a dual character. The major drop showed a non-wetting character, however, a substantial amount of a transparent phase which showed strong wetting characteristics was found beside the drop. Figure 9 shows two views of this specimen. The blocky macrocrystalline appearance together with the presence of the highly fluid wetting phase suggested that during the cooling process fractional crystallization had taken place. Thus a



a. Shows evidence of gas evolution

(17x)



b. Reaction with substrate

(19x)

Figure 7. Sessile Drop Specimen B-1  
(60%  $Y_2O_3$  - 20  $Al_2O_3$  - 20  $SiO_2$ )



a. Silhouette showing small wetting angle

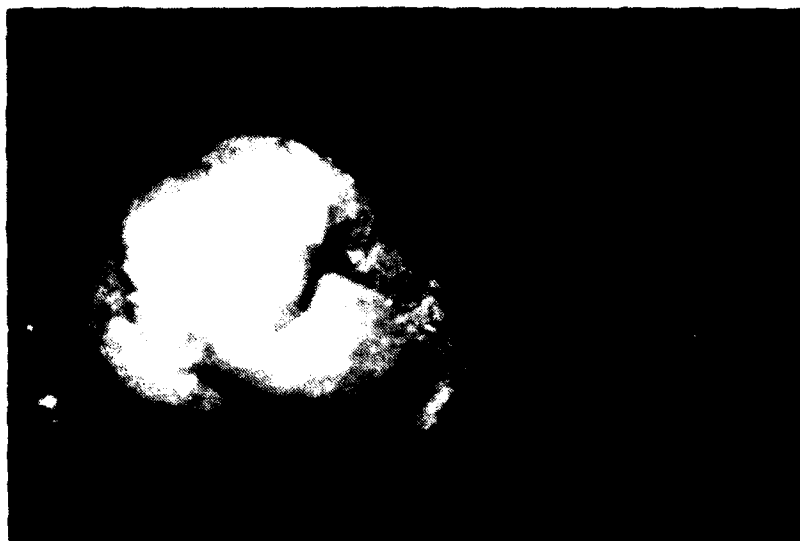
(13x)



b. Craters apparently caused by gas evolution

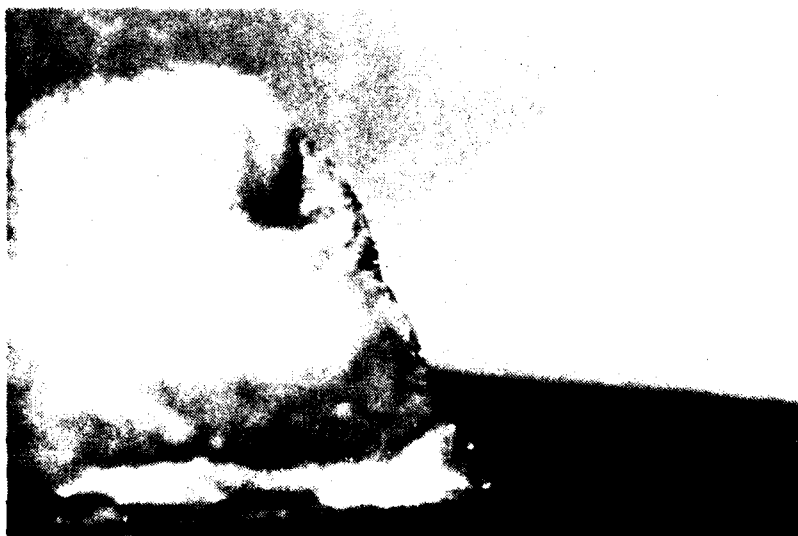
(16x)

Figure 3. Sessile Drop Specimen B-2  
(60  $\text{Y}_2\text{O}_3$  - 20  $\text{Al}_2\text{O}_3$  - 20  $\text{SiO}_2$ )



a. Note block-like structure and evidence of liquid wetting substrate

(13x)



b. Silhouette view

(17x)

Figure 9. Sessile Drop Specimen C-1  
(42%  $Y_2O_3$  - 38  $Al_2O_3$  - 20  $SiO_2$ )

second specimen was run with a faster cooling rate to a temperature below the solidus.

The second specimen, C2, is shown in Figure 10. Note the much more spherical shape and the absence of a second fluid or wetting phase at the juncture between the drop and the substrate as shown in Figure 10(b). The x-ray diffraction analyses of Specimen C1 and C2 showed YAG,  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ - $\text{SiO}_2$ .

Specimen D1 consisted of an additive of composition  $37\text{Y}_2\text{O}_3$ - $28\text{Al}_2\text{O}_3$ - $35\text{SiO}_2$  in contact with a CVD  $\text{Si}_3\text{N}_4$  substrate. In this case, the additive wet very well, giving wetting angles of  $33^\circ$  and  $48^\circ$ . The drop appeared completely transparent and noncrystalline. Unfortunately, the only photograph available is the silhouette photo shown in Figure 11. The photographs of the next specimen, however, illustrate the nature of the drop very well.

Specimen D2 was the same composition as D1 but was in contact with a polished reaction bonded silicon nitride (RBSN) surface. Figure 12 shows this specimen from above and in silhouette. It is clear that the additive did not wet the substrate. The noncrystalline character of the drop is apparent. X-ray diffraction analysis further confirms the noncrystalline nature of the additive material after test. In neither Specimen D1 nor D2 was a crystalline diffraction pattern observed after test. It should be noted in addition that this composition was non-crystalline after the additive pre-reaction heat treatment as shown in Table III.



(13x)



(20x)

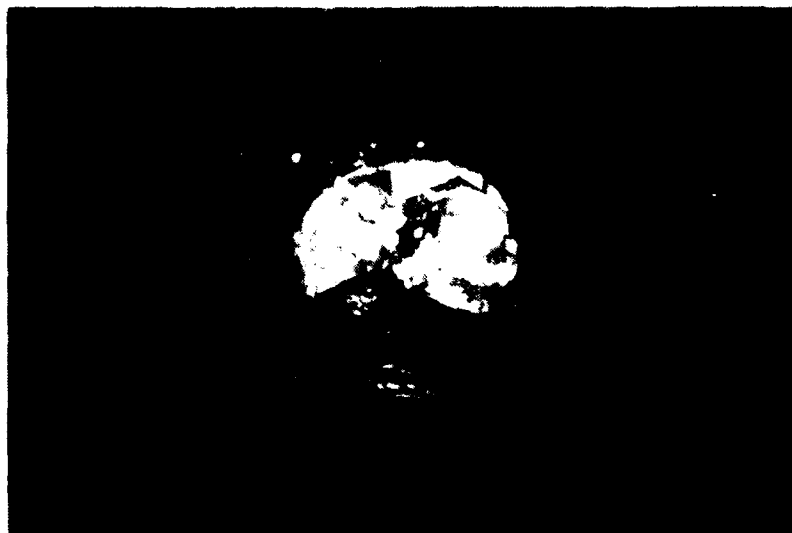
Figure 10. Sessile Drop Specimen C-2  
(42%  $Y_2O_3$  - 38  $Al_2O_3$  - 20  $SiO_2$ )





(8x)

Figure 11. Sessile Drop Specimen D-1  
(37  $\text{Y}_2\text{O}_3$  - 28  $\text{Al}_2\text{O}_3$  - 35  $\text{SiO}_2$ )



(13x)



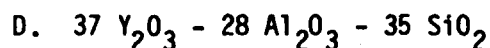
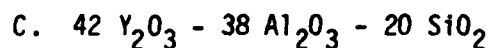
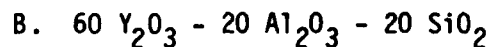
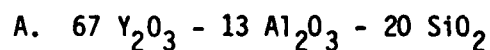
(26x)

Figure 12. Sessile Drop Specimen D-2  
 (37%  $Y_2O_3$  - 28  $Al_2O_3$  - 35  $SiO_2$  on RBSN)

## B. Results of the Penetration Experiments

### 1. Visual Examination

A total of five experimental runs were made in the study of penetration of additives in the reaction bonded silicon nitride. The additive compositions studied were the same as those used in the sessile drop experiments. These were:



In four of the five experimental runs the specimen cavities were filled with identical compositions. In one case two different compositions were used. Table V gives the experimental conditions of each of the test runs and some general observations made visually and with the aid of a low-power optical microscope.

### 2. Polished-Section, Reflected Light Microscopy

A number of sections were cut through the specimen cavities to evaluate the penetration behavior of the additives by observation of the section by reflected-light microscopy. The low density of the reaction-bonded material makes polishing of the sections very difficult and the resultant photographs of low quality. As a result, the only specimen which yielded significant photographs of these sections was that of Run B, the  $60\text{Y}_2\text{O}_3\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{SiO}_2$  specimen which showed wetting

TABLE V

Conditions and General Results of Penetration Experiments

Run A1 (Figure 13)

Additive:  $67 \text{ Y}_2\text{O}_3 - 13 \text{ Al}_2\text{O}_3 - 20 \text{ SiO}_2$ ;  $T_L^* = 1700^\circ\text{C}$

Temperature/Hold Time:  $1725^\circ\text{C}/1 \text{ hour}$

General Observations: Additive interacted with specimen block lid.

Run A2 (Figure 14)

Additive:  $67 \text{ Y}_2\text{O}_3 - 13 \text{ Al}_2\text{O}_3 - 20 \text{ SiO}_2$ ;  $T_L = 1700^\circ\text{C}$

Temperature/Hold Time:  $1710^\circ\text{C}/1 \text{ hour}$

General Observations: Nearly spherical, nonwetting drop remaining in cavity. No apparent interaction with specimen block. Small black beads adhering to drop. Drop appears smooth and shiny, but opaque.

Run B (Figure 15)

Additive:  $60 \text{ Y}_2\text{O}_3 - 20 \text{ Al}_2\text{O}_3 - 20 \text{ SiO}_2$ ;  $T_L = 1625^\circ\text{C}$

Temperature/Hold Time:  $1750^\circ\text{C}/1 \text{ hour}$

General Observations: Additive appears to have completely penetrated the specimen block, the only residue appearing in the cavity being small black spheres.

Run C1 (Figure 16)

Additive:  $42 \text{ Y}_2\text{O}_3 - 38 \text{ Al}_2\text{O}_3 - 20 \text{ SiO}_2$ ;  $T_L = 1600^\circ\text{C}$

Temperature/Hold Time:  $1650^\circ\text{C}/1 \text{ hour}$

General Observations: Crystalline material in central region with glassy appearing material surrounding. Glassy material appears to wet cavity. Black needle-like crystals appear to be artifacts since they do not appear in any other specimen including re-run C2.

\* Liquidus Temperature

TABLE V--continued

Run C2 (Figure 17)

Additive: 42  $\text{Y}_2\text{O}_3$  - 38  $\text{Al}_2\text{O}_3$  - 20  $\text{SiO}_2$ ;  $T_L = 1600^\circ\text{C}$

Temperature/Hold Time:  $1710^\circ\text{C}/1$  hour

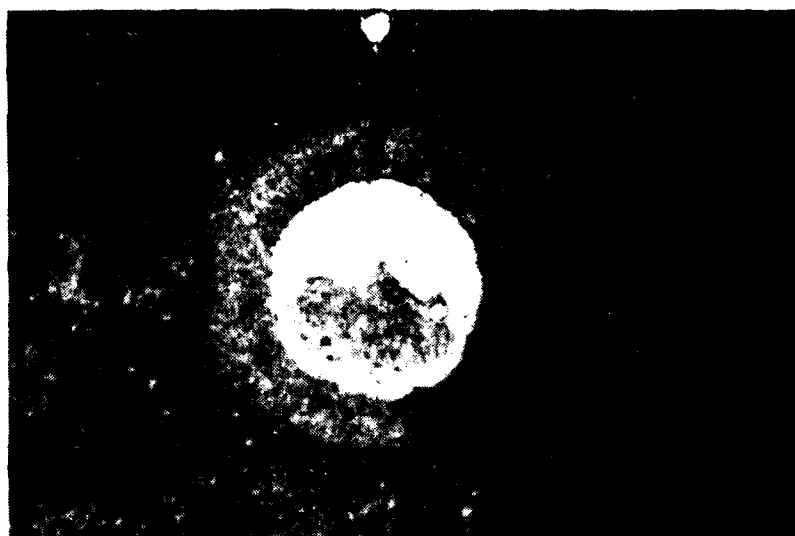
General Observations: Strong interaction of additive with cavity.  
Appearance of liquid running out of crystalline pellet or head. Interaction zone shows numerous small black heads.

Run D (Figure 18)

Additive: 37  $\text{Y}_2\text{O}_3$  - 28  $\text{Al}_2\text{O}_3$  - 35  $\text{SiO}_2$ ;  $T_L = 1400^\circ\text{C}$

Temperature/Hold Time:  $1610^\circ\text{C}/1$  hour

General Observations: Transparent drop which shows intermediate wetting characteristics ( $\theta \approx 90^\circ$ ). No apparent interaction with substrate. Faint dark ring surrounding specimen cavity.



(10x)

Figure 13. Penetration Specimen A-1  
(67%  $Y_2O_3$  - 13  $Al_2O_3$  - 20  $SiO_2$ )

Note reaction with lid



a. Residual additive in cavity

(10.5x)



b. Residual additive in ovoid cavity

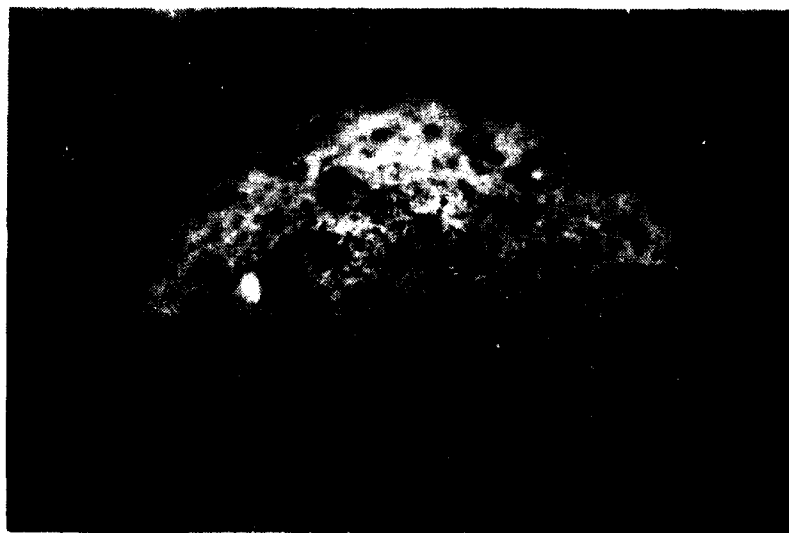
(15x)

Figure 14. Penetration Specimen A-2  
(67  $\text{Y}_2\text{O}_3$  - 13  $\text{Al}_2\text{O}_3$  - 20  $\text{SiO}_2$ )



a. Note apparent penetration of upper surface

(15x)



b. Note lack of residual material and black beads

(18x)

Figure 15. Penetration Specimen B  
(60  $Y_2O_3$  - 20  $Al_2O_3$  - 20  $SiO_2$ )





a. Note apparent two-phase structure

(10.5x)



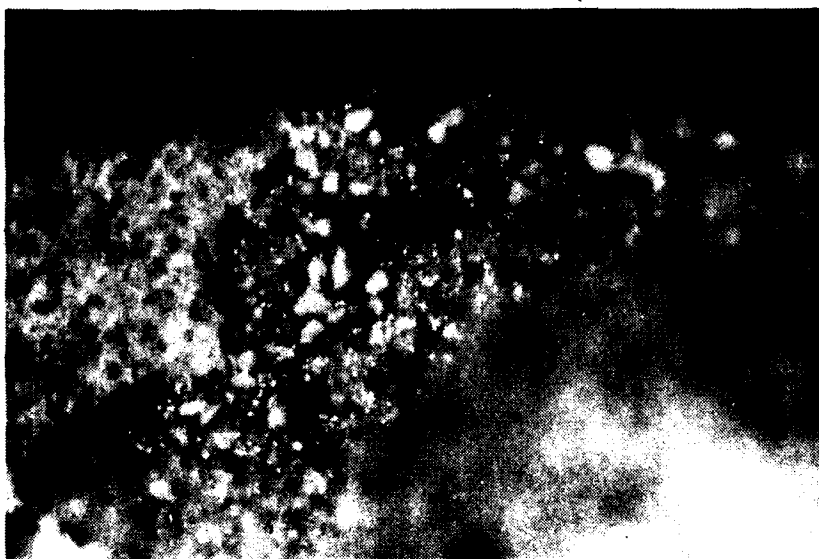
b. Needle-like artifacts

(42x)

Figure 16. Penetration Specimen C-1  
(42%  $Y_2O_3$  - 38  $Al_2O_3$  - 20  $SiO_2$ )

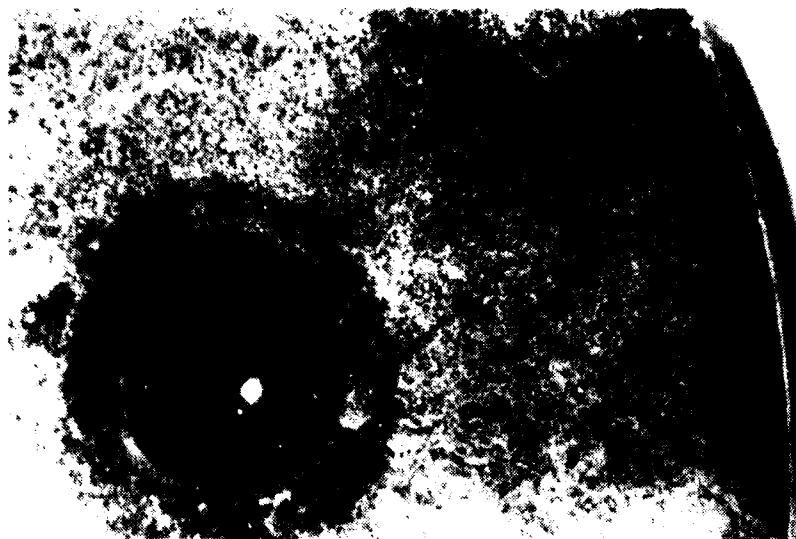


a. Further evidence of two-phase structure (10x)



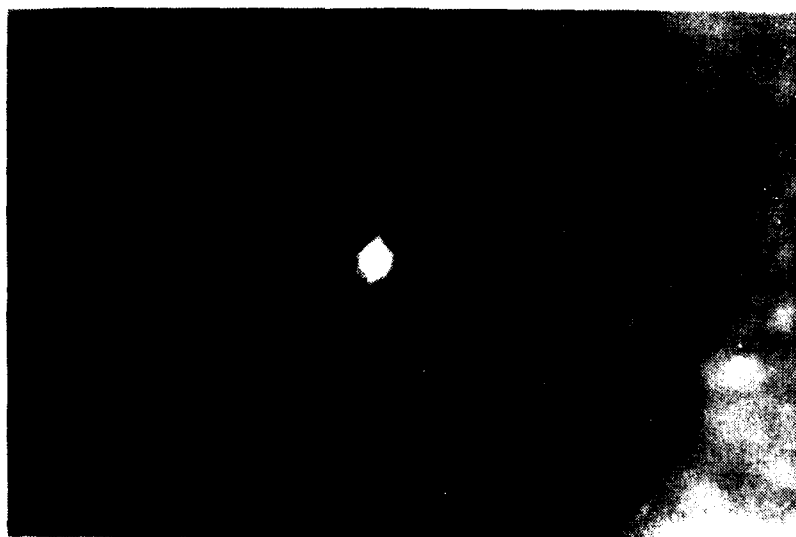
b. Shows strong reactivity of additive (48x)

Figure 17. Penetration Specimen C-2  
 (42  $Y_2O_3$  - 38  $Al_2O_3$  - 20  $SiO_2$ )



a. Note apparent penetration ring at top surface

(10.5x)



b. Note transparency

(17.5x)

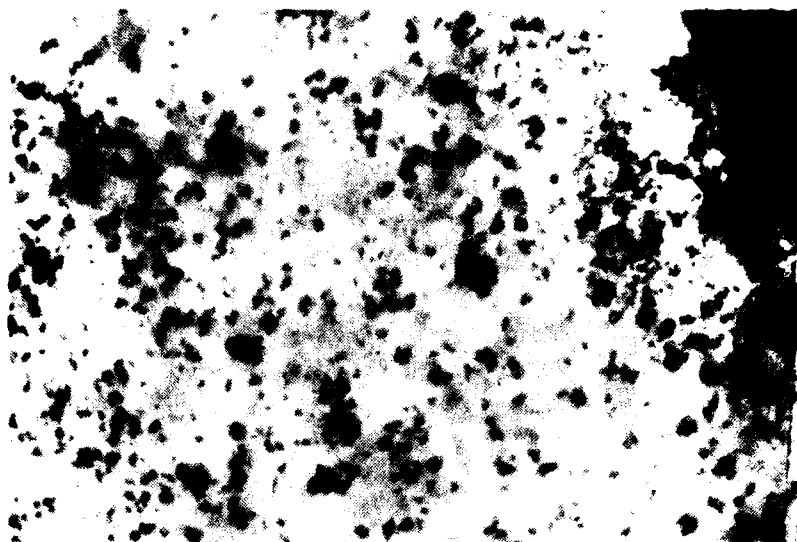
Figure 18. Penetration Specimen D  
(37  $\text{Y}_2\text{O}_3$  - 23  $\text{Al}_2\text{O}_3$  - 35  $\text{SiO}_2$ )

and good penetration under visual examination. This specimen is shown in Figure 19 and 20. These sections indicate a penetration of approximately 0.4 millimeters.

### 3. X-ray Microanalysis

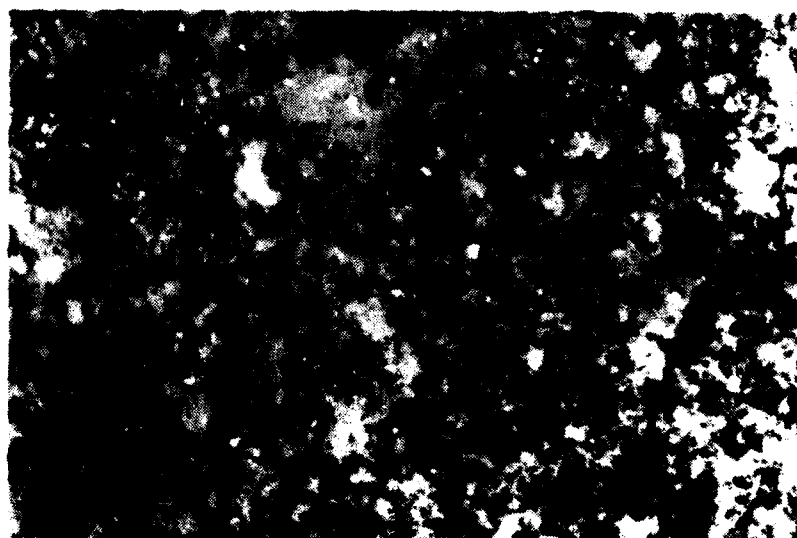
X-ray microanalysis proved valuable only in a limited way. Attempts to measure penetration depths on polished sections of the specimen blocks were unsuccessful. Neither aluminum nor yttrium variation could be seen in the sections beyond 1 mm from the edge of the cavity and this was only possible in the experiment in which all of the additive apparently penetrated the specimen block. Attempts to determine changes in composition of the additive material remaining in the cavity relative to the starting material were also unsuccessful. The aluminum to yttrium ratio for the pretest and posttest material in the cavities varied only slightly for those tests with considerable residual material remaining in the cavity. In the one case which showed considerable penetration, the aluminum to yttrium ratio increased five-fold when comparing the starting powder to the inside surface of the cavity. (The specimens were sectioned to allow analysis of the inside surfaces).

X-ray microanalysis was able to identify the black spherical beads seen in at least two of the specimens as described above. These appear to be silicon with a very high iron content. The spherical shape suggests they were molten at the test temperature and were perhaps displaced from the silicon nitride structure by additive penetrations



a. Near Cavity (upper right)

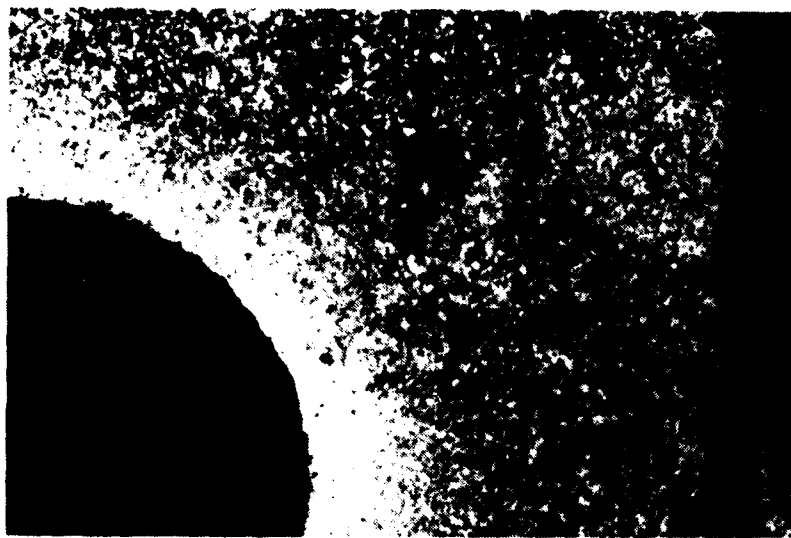
(405x)



b. 3 mm from hole

(405x)

Figure 19. Polished Section of Penetration  
Specimen B  
(60  $Y_2O_3$  - 20  $Al_2O_3$  - 20  $SiO_2$ )



(26x)

Figure 20. Penetration Specimen B  
Polished Section

since they are most evident in specimens B and C2 which showed the strongest wetting or penetration behavior.

### C. Discussion of Results

The behavior of the limited set of additive compositions studied in this work was in general negative with respect to the implicit hypothesis held initially that the additives would wet the substrate silicon nitride, the only question being which wet best. Only one composition, the 60 yttria-20 alumina showed good wetting of the CVD substrate when in the totally liquid state. The 42 yttria-38 alumina did not wet while the residual liquid present upon primary crystallization does wet. Nor does the high yttria specimen (67 yttria-13 alumina) wet the substrate. Thus, for a sintering process employing a sintering aid which contains approximately 20 percent silica contributed by the oxygen content of the starting powder, only a relatively narrow range of yttria concentration provides a wetting liquid. This range is somewhere between 42  $Y_2O_3$ -38  $Al_2O_3$ -20  $SiO_2$  and 67  $Y_2O_3$ -13  $Al_2O_3$ -20  $SiO_2$ . Additional work is necessary to more closely define the range. Even though a higher  $SiO_2$  concentration may give better wettability as shown by the wetting behavior of the 35 percent  $SiO_2$  specimen on the CVD substrate, it is probable that high silica compositions will lead to non-crystalline grain boundary phases at service temperatures with attendant creep and fracture difficulties. It is therefore felt that further work should be conducted primarily the lower silica concentrations.

The inconclusive evidence of bubble and crater formation in the 60  $\text{Y}_2\text{O}_3$ -20  $\text{Al}_2\text{O}_3$ -20  $\text{SiO}_2$  sessile drop specimen is unsupported by the penetration experiments since that composition left no residual additive in the specimen cavity. There is some additional evidence which was gained in exploratory attempts to run an experiment in which the sessile drop could be observed optically. These preliminary results also suggest a gaseous reaction at the additive-silicon nitride interface. The presence of bubbles within the additive drop implies a gaseous reaction product of greater than one atmosphere since the system pressure is one atmosphere. The identity of the gaseous product is unknown but the high pressures would favor either nitrogen or oxygen. It seems improbable that more complex species would have pressures as high as one atmosphere, although it could be possible.

The presence of a reactive liquid in relatively large proportions which remained after primary crystallization of the 42 $\text{Y}_2\text{O}_3$ -38 $\text{Al}_2\text{O}_3$ -20 $\text{SiO}_2$  composition was observed in both the sessile drop and penetration studies. The implications of this behavior are rather intriguing. It may be possible to use the secondary liquid as a sintering aid, either by formulating a batch which duplicates the secondary liquid composition or by controlling the temperature carefully to maintain the secondary liquid in the presence of the primary crystals. The effect of the primary crystals on the sintering process is unknown, however, the system should be looked at more clearly.



## V. Conclusions and Recommendations

It is felt that this work has shown that the behavior of this additive system is sufficiently complex that additional work would be valuable. The following conclusions and recommendations are meant to assist in further work rather than to stand as final statements in this area of endeavor.

1. The implicit hypothesis of a relatively benign liquid phase which wets silicon nitride over a wide range of yttrium contents appears to be untrue. The limited indications suggest that the wettability range is small and that the compositions are reactive to the substrate even though they do not spread (wet) readily.
2. A much larger experimental data base is necessary if this relatively complex behavior is to be understood.
3. The experiments should be conducted in a manner which allows direct visual observation.
4. Each composition should be evaluated over a range of temperatures.
5. The wetting behavior of the  $60Y_2O_3-20Al_2O_3-20SiO_2$  composition bears more study. On the basis of these limited results, this is the only strongly wetting composition which was low enough in  $SiO_2$  to make a crystalline grain boundary phase probable.

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